

Constructing non-equilibrium statistical ensemble formalism based on Subdynamics

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Abstract

In this work, we present a general non-equilibrium ensemble formalism based on the subdynamic equation (SKE). The constructing procedure is to use a similarity transformation between Gibbsian ensemble formalism and the non-equilibrium ensemble formalism. The obtained density distribution is a projected one that can represent essence part of (irreversible) evolution of the density distribution, by which a generalized reduced density distribution for the quantum canonical ensembles is studied and applications in Cayley tree and spin network are discussed.

I. INTRODUCTION

Since Gibbs synthesized a general equilibrium statistical ensemble theory, many theorists have attempted to generalize the Gibbsian theory to non-equilibrium phenomena domain, however the status of the theory of non-equilibrium phenomena can not be said as firm as well established as the Gibbsian ensemble theory, although great works have been done by numerous authors^{[1]-[9]}. The number of references along this line of research is too numerous to cite them all here, we just mention three significant progresses: the relevant ensembles theory presented by Zubarev, Morozov and Röpke^[10], the Jaynes' predictive statistical mechanics approach^[11], and the generalized Gibbsian ensembles theory based on the Boltzmann kinetic equation presented by Chan Eu^[12]. So far the obtained non-equilibrium statistical density distribution formulas for the ensembles do not satisfy the original Liouville equation. Some researchers for that reason believe that the Liouville equation must have an extra term which satisfies a set of conditions assuring its irreversibility and existence of conservation laws if the Gibbs ensemble theory is generalized to the non-equilibrium phenomena domain based on the Liouville equation. But how is it possible to find this extra term which possesses universal irreversible characteristic to satisfy numerous requirements from a large body of models? This means the efforts of many schools until now have not produced a universal ensemble theory for non-equilibrium phenomena which is comparable to the Gibbsian ensemble theory for equilibrium phenomena.

In this work, we present a non-equilibrium statistical ensemble formalism based on a subdynamic kinetic equation (SKE) rooted from the Brussels-Austin school^{[13]-[14]} and followed by some up-to-date works^{[16]-[17]}. The advantage of the scheme is that SKE intertwines with the original Liouville equation by a similarity transformation. If the similarity transformation is non-unitary, the SKE can describe the irreversible process, otherwise, it describes the reversible process as an equivalent equation of the original Liouville equation. Although there exist several different approaches to construct SKE, that can be found in some publications^{[13]-[17]}, here considering reader may be not familiar with formalism of subdynamics, we try to start from an update-introduction.

II. SUBDYNAMICS FORMALISM

Let a quantum system S be coupled (may be strongly) to a thermal reservoir B , $H_S(t)$, H_B , and H_{int} denote the Hamiltonian of the system S , the Hamiltonian of the thermal reservoir B , and the interaction between S and B , respectively. The total Hamiltonian $H(t)$ of the system plus the reservoir can be expressed as $H_S(t) \otimes I_B + I_S \otimes H_B + H_{int}$, and the corresponding quantum Schrödinger equation and Liouville equation are

$$i \frac{\partial f}{\partial t} = H(t) f, \quad (1)$$

and

$$i \frac{\partial \rho}{\partial t} = [H(t), \rho], \quad (2)$$

where $\rho = |f\rangle \langle f|$ is a density operator for the total system. Then one can introduce an orthonormal projector P_{kj} with $Q_{kj} = 1 - P_{kj}$ so that

$$P_{kj} H(t) P_{kj} = P_{kj} H_0(t) P_{kj}, \quad (3)$$

$$P_{kj} H(t) Q_{kj} = P_{kj} H_{int} Q_{kj}. \quad (4)$$

Then the total Hamiltonian $H(t) = H_S(t) + H_B + H_{in}$ can be expressed as

$$H(t) = PH(t)P + PH(t)Q + QH(t)P + QH(t)Q, \quad (5)$$

and a corresponding projected matrix is represented as

$$\begin{pmatrix} P_{kj} H(t) P_{kj} & Q_{kj} H(t) P_{kj} \\ P_{kj} H(t) Q_{kj} & Q_{kj} H(t) Q_{kj} \end{pmatrix}. \quad (6)$$

The eigenvalue problem can be written as

$$\begin{pmatrix} P_{kj} H(t) P_{kj} & Q_{kj} H(t) P_{kj} \\ P_{kj} H(t) Q_{kj} & Q_{kj} H(t) Q_{kj} \end{pmatrix} \begin{pmatrix} \phi_{kj} \\ \phi_{k'j'} \end{pmatrix} = \begin{pmatrix} E_{kj}(t) & 0 \\ 0 & E_{k'j'}(t) \end{pmatrix} \begin{pmatrix} \phi_{kj} \\ \phi_{k'j'} \end{pmatrix}, \quad (7)$$

giving

$$P_{kj} H(t) P_{kj} \phi_{kj} + P_{kj} H(t) Q_{kj} \phi_{k'j'} = E_{kj}(t) \phi_{kj}, \quad (8)$$

$$Q_{kj} H(t) P_{kj} \phi_{kj} + Q_{kj} H(t) Q_{kj} \phi_{k'j'} = E_{k'j'}(t) \phi_{k'j'}. \quad (9)$$

From Eqs.(9) and (8), one can solve $\phi_{k'j'}$ and ϕ_{kj} respectively as

$$\begin{aligned}\phi_{k'j'} &= (E_{k'j'}(t) - Q_{kj}H(t)Q_{kj})^{-1}Q_{kj}H(t)P_{kj}\phi_{kj} \\ &= C_{kj}\phi_{kj},\end{aligned}\tag{10}$$

$$\begin{aligned}\phi_{kj} &= (E_{kj}(t) - P_{kj}H(t)P_{kj})^{-1}P_{kj}H(t)Q_{kj}\phi_{k'j'} \\ &= C_{k'j'}\phi_{k'j'}.\end{aligned}\tag{11}$$

Substituting Eq.(10) into Eq.(8) and Eq.(11) into Eq.(9) respectively gives

$$(P_{kj}H(t)P_{kj} + P_{kj}H(t)C_{k'j'}(t))\phi_{kj} = \Theta_{k'j'}(t)\phi_{kj} = E_{kj}\phi_{kj},\tag{12}$$

$$(Q_{kj}H(t)P_{kj} + Q_{kj}H(t)C_{kj}(t))\phi_{k'j'} = \Theta_{kj}(t)\phi_{k'j'} = E_{k'j'}(t)\phi_{k'j'},\tag{13}$$

where introducing a creation (destruction) correlation operator (as a type of resolvent) as

$$C_{kj}(t) = Q_{kj}C_{kj}(t)P_{kj} = (E_{k'j'}(t) - Q_{kj}H(t)Q_{kj})^{-1}Q_{kj}H(t)P_{kj},\tag{14}$$

$$C_{k'j'}(t) = P_{kj}C_{k'j'}(t)Q_{kj} = (E_{kj}(t) - P_{kj}H(t)P_{kj})^{-1}P_{kj}H(t)Q_{kj}.\tag{15}$$

This shows that the $(\phi_{kj}, \phi_{k'j'})$ are the eigenvectors of the $\Theta_{k'j'}(t)$ and $(E_{kj}(t), E_{k'j'}(t))$ are the eigenvalues of $\Theta_{k'j'}(t)$ and $H(t)$. This allows one to presume that the eigenvector of $H(t)$ is given by f_{kj} with the same eigenvalue $E_{kj}(t)$,

$$H(t) \begin{pmatrix} |f_{kj}\rangle \\ |f_{k'j'}\rangle \end{pmatrix} = \begin{pmatrix} Z_{kj}(t) |f_{kj}\rangle \\ Z_{k'j'}(t) |f_{k'j'}\rangle \end{pmatrix},\tag{16}$$

then one can find by using Eqs.(7-13),

$$\begin{aligned}\begin{pmatrix} P_{kj}H(P_{kj} + Q_{kj})f_{kj} \\ Q_{kj}H(P_{kj} + Q_{kj})f_{kj} \end{pmatrix} &= \begin{pmatrix} P_{kj}HP_{kj} & P_{kj}HQ_{kj} \\ Q_{kj}HP_{kj} & Q_{kj}HQ_{kj} \end{pmatrix} \begin{pmatrix} P_{kj}f_{kj} \\ Q_{kj}f_{kj} \end{pmatrix} \\ &= \begin{pmatrix} E_{kj}(t) & 0 \\ 0 & E_{k'j'}(t) \end{pmatrix} \begin{pmatrix} \phi_{kj} \\ \phi_{k'j'} \end{pmatrix} \\ &= \begin{pmatrix} \Theta_{k'j'} & 0 \\ 0 & \Theta_{kj} \end{pmatrix} \begin{pmatrix} \phi_{kj} \\ \phi_{k'j'} \end{pmatrix}.\end{aligned}\tag{17}$$

This gives some interesting relations as

$$P_{kj}f_{kj} = \phi_{kj} = C_{kj}\phi_{k'j'} = C_{kj}Q_{kj}f_{kj},\tag{18}$$

$$Q_{kj}f_{kj} = \phi_{k'j'} = C_{k'j'}\phi_{kj} = C_{k'j'}P_{kj}f_{kj},\tag{19}$$

and

$$f_{kj} = P_{kj}\phi_{kj} + Q_{kj}\phi_{k'j'} = (P_{kj} + C_{k'j'})\phi_{kj}. \quad (20)$$

Using Eq.(19), by introducing $\Pi_{kj}(t) = |f_{kj}(t)\rangle\langle f_{kj}(t)|$ as an eigen-projector of $H(t)$, one can construct a Schrödinger type of kinetic equation for each projected state $P_{kj}\Pi_{kj}(t)|\phi(t)\rangle$ as

$$\begin{aligned} i\frac{\partial}{\partial t}P_{kj}\Pi_{kj}(t)|\phi(t)\rangle &= iP_{kj}\left[\left(\frac{\partial}{\partial t}\Pi_{kj}(t)\right)|\phi(t)\rangle + \Pi_{kj}(t)\frac{\partial}{\partial t}|\phi(t)\rangle\right] \\ &= P_{kj}\{[H(t), \Pi_{kj}(t)]|\phi(t)\rangle + \Pi_{kj}(t)H(t)|\phi(t)\rangle\} \\ &= P_{kj}H(t)(P_{kj} + Q_{kj})\Pi_{kj}(t)|\phi(t)\rangle \\ &= P_{kj}H(t)(P_{kj} + C_{kj}(t))\Pi_{kj}(t)|\phi(t)\rangle, \end{aligned} \quad (21)$$

where, for more generality, $\Pi_{kj}(t)$ can be understood as $|f_{kj}(t)\rangle\langle\tilde{f}_{kj}(t)|$ in which $f_{kj}(t) \in \Phi$ (dense subspace) and $\tilde{f}_{kj}(t) \in \Phi^\times$ (generalized dual subspace of Φ) are defined in a Rigged Hilbert space, $\Phi \subset \mathcal{H} \subset \Phi^\times$. This can generally provide a Schrödinger type of subdynamics kinetic equation (SSKE) expressed as

$$i\frac{\partial}{\partial t}\phi_{proj}(t) = \Theta(t)\phi_{proj}(t), \quad (22)$$

$$-i\frac{\partial}{\partial t}\tilde{\phi}_{proj}(t) = \Theta(t)\tilde{\phi}_{proj}(t), \quad (23)$$

with

$$\Theta(t) = \sum_{kj} P_{kj}H(t)(P_{kj} + C_{kj}(t)), \quad (24)$$

where ϕ_{proj} and $\tilde{\phi}_{proj}(t)$ are defined as

$$|\phi_{proj}(t)\rangle = \sum_{kj} P_{kj}\Pi_{kj}(t)|\phi(t)\rangle, \quad (25)$$

$$\langle\tilde{\phi}_{proj}(t)| = \sum_{kj} \langle\tilde{\phi}(t)|P_{kj}\Pi_{kj}(t), \quad (26)$$

and $\phi(t)$ or $\tilde{\phi}(t)$ is a solution of the original Schrödinger equation in the Rigged Hilbert space. Furthermore, by replacing $\rho_{proj}(t) = |\phi_{proj}(t)\rangle\langle\tilde{\phi}_{proj}(t)|$, and using the above SSKE, a Liouvillian type of kinetic equation (LSKE) can be derived by

$$\begin{aligned} i\frac{\partial}{\partial t}\rho_{proj}(t) &= \left(i\frac{\partial}{\partial t}|\phi_{proj}(t)\rangle\right)\langle\phi_{proj}(t)| + |\phi_{proj}(t)\rangle\left(i\frac{\partial}{\partial t}\langle\phi_{proj}(t)|\right) \\ &= \Theta(t)|\phi_{proj}(t)\rangle\langle\phi_{proj}(t)| - |\phi_{proj}(t)\rangle\langle\phi_{proj}(t)|\Theta(t) \\ &= [\Theta(t), \rho_{proj}(t)]. \end{aligned} \quad (27)$$

The construction of SSKE or LSKE in subspace can be related to the original Schrödinger or Liouville equation^{[13],[16]}. For instance, using the relation (20) one have the spectral representation of $H(t)$ related to $\Theta(t)$ as

$$\begin{aligned} H(t) &= \sum_{kj} Z_{kj}(t) |f_{kj}\rangle \langle \tilde{f}_{kj}| \\ &= \sum_{kj} Z_{kj}(t) (P_{kj} + C_{kj}(t)) |\phi_{kj}\rangle \langle \phi_{kj}| (P_{kj} + D_{kj}(t)) \\ &= \Omega(t) \Theta(t) \Omega^{-1}(t), \end{aligned} \quad (28)$$

where $D_{kj}(t) = C_{kj}^\dagger(t)$, and $\Omega(t) = \sum_{kj} (P_{kj} + C_{kj}(t))$. The creation operator, $C_\nu = \frac{1}{Z - Q_\nu H Q_\nu} Q_\nu H P_\nu = (D_\nu)^\dagger$, creates the Q_ν -part of Π_ν from the P_ν -part. While $\Theta = H_0 + \lambda H_1 C$ is called collision operator^[18]. The physical meaning of ρ_{proj} is that it represents the "vacuum" part of the "dynamic" part of the original density operator ρ , which describes the essence of (irreversible) evolution of the density ρ in its own subspace^[19]. The second order approximation of Θ with respect to λ corresponds to the Master equation^[15]. Moreover, the Boltzmann, Pauli, and Fokker-Planck equations of kinetic theory and Brownian motion can also be derived by using some approximation of Θ ^[19]. The creation operator and destruction operator can also be calculated by using operator algebra to perform several different approaches. One of interested approaches to obtain the recurrent formulas is

$$C_\nu = i \int_0^{\pm\infty} d\tau U(\tau) \lambda (C_\nu - Q_\nu) H (P_\nu + C_\nu) U(-\tau), \quad (29)$$

$$D_\nu = i \int_0^{\pm\infty} d\tau U(\tau) \lambda (P_\nu + D_\nu) H (P_\nu - D_\nu P_\nu) U(-\tau), \quad (30)$$

where defining $U(\tau) = \exp(-\tau H_0)$.

III. NON-EQUILIBRIUM STATISTICAL ENSEMBLES

A marvelous remark is that the SKE seems to have the general property to approach various kinetic equations or Master equations, which is beyond the original Liouville equation. As previous mentioned, the Brussels-Austin group have developed many important works for SKE in last two decades and have found that SKE can intertwine with the original Liouville equation by a similarity operator. If the similarity operator is unitary, the

SKE is reversible, as an equivalent representation of Liouville equation; if the similarity operator is not unitary, the SKE is irreversible and the corresponding evolution is not time symmetric. This means that the SKE can be as an appropriate kinetic equation to describe the irreversible process, in which the evolution operator is non-unitary on generalized functional space which is beyond the traditional Hilbert (or Liouville) space. This motivates one to propose using the SKE to construct a non-equilibrium statistical ensemble theory. The constructing procedure may be quite simple by using the "similarity transformation corresponding" between Gibbsian ensembles formalism based on the Liouville equation and the non-equilibrium ensembles formalism based on SKE: if the Hamiltonian corresponding to an expectation value, then the corresponding expectation of the Θ operator should be

$$Tr(H\rho) = \langle H \rangle \longrightarrow Tr(\Theta P \Pi \rho) = \langle \Theta \rangle, \quad (31)$$

thus the related entropy tends to extremum, this allows one to present (by extension) a new canonical ensemble distribution $\rho(\theta_k)$ which is "vacuum" of "dynamic part" of the original $\rho(E_k)$, as expressed by Balescu's book [19],

$$\rho(E_k) = Z^{-1}(\beta, V, N) \exp(-\beta E_k) \longrightarrow \rho(\theta_k) = Z^{-1}(\beta_{proj}, V_{proj}, N_{proj}) \exp(-\beta_{proj} \theta_k) \quad (32)$$

with the partition functions as

$$Z(\beta, V, N) = \sum_k \exp(-\beta E_k) \longrightarrow Z(\beta_{proj}, V_{proj}, N_{proj}) = \sum_k \exp(-\beta_{proj} \theta_k), \quad (33)$$

$$\beta = (k_B T)^{-1} \longrightarrow \beta_{proj} = (k_B T_{proj})^{-1}, \quad (34)$$

where θ_k is an eigenvalue of Θ , β_{proj} is extended as function of position and time. In fact, suppose the density distribution in quantum canonical system is given by

$$\rho(E_{kj}) = \left\{ \frac{\exp(-\beta E_{kj})}{\sum_{kj} \exp(-\beta E_{kj})} \right\}, \quad (35)$$

which gives the density operator ρ as

$$\begin{aligned} \rho &= \sum_{kj} |f_{kj}\rangle \frac{\exp(-\beta E_{kj})}{\sum_{kj} \exp(-\beta E_{kj})} \langle f_{kj}| \\ &= \frac{1}{Tr \exp(-\beta H)} \exp(-\beta H) \sum_{kj} |f_{kj}\rangle \langle f_{kj}| \\ &= \frac{\exp(-\beta H)}{Tr \exp(-\beta H)}. \end{aligned} \quad (36)$$

Thus using the similarity transformation Ω one can obtain a projected density operator ρ_{proj} as

$$\begin{aligned}\rho_{proj} &= \Omega^{-1} \rho \Omega = \Omega^{-1} \frac{\exp(-\beta H)}{\text{Tr} \exp(-\beta H)} \Omega \\ &= \frac{\exp(-\Omega^{-1} \beta \Omega \Omega^{-1} H \Omega)}{\text{Tr} \exp(-\Omega^{-1} \beta \Omega \Omega^{-1} H \Omega)} \\ &= \frac{\exp(-\beta_{proj} \Theta)}{\text{Tr} \exp(-\beta_{proj} \Theta)}.\end{aligned}\tag{37}$$

This gives a precise formula of the quantum canonical ensemble for a projected density operator ρ_{proj} , which can be considered as generalizing the equilibrium quantum canonical ensembles formula to the non-equilibrium quantum canonical ensembles formula in the sense as (1) if the similarity operator is unitary, then the new formula is just an effective representation of the old equilibrium quantum canonical ensembles formula because Θ or H has the same spectral structure, (2) if the similarity operator is non-unitary, then the new formula is an extension of the old formula and the spectrum of Θ may appear to have complex spectral structure that is impossible to get from the original self-adjoint operator H in the Hilbert space, which represents kind of non-equilibrium quantum canonical ensembles formula and reflects irreversibility of the system, and (3) if the similarity operator can be deduced by some approximations, such as Markovian/non-markovian approximations, then the new formula can expose some non-equilibrium characteristics, which can not be gained from the equilibrium quantum ensemble formulas.

Thus it is obvious that the preceding constructed quantum formalism for density operator $\rho(\theta_k)$ can be extended to the classical statistical canonical ensemble by

$$\rho(\theta_k) = Z^{-1}(\beta_{proj}, V_{proj}, N_{proj}) \exp(-\beta_{proj} \theta_k)\tag{38}$$

with

$$Z(\beta_{proj}, V_{proj}, N_{proj}) = \int \exp(-\beta_{proj} \Theta) dx.\tag{39}$$

In the same way, the non-equilibrium grand canonical ensembles distribution can also be constructed by

$$\rho(\theta_k) = Z^{-1}(\beta_{proj}, \mu_{proj}, V_{proj}) \exp[-\beta_{proj} \theta_k - \mu_{proj} N_{proj}],\tag{40}$$

where the partition function is given by

$$Z(\beta_{proj}, \mu_{proj}, V_{proj}) = \sum_k \int \exp[-\beta_{proj} \theta_k - \mu_{proj} N_{proj}].\tag{41}$$

Furthermore, the general canonical ensembles distribution may be written by

$$\rho = Z^{-1} \exp \left[-\beta_{proj} \theta_k - \mu_{proj} N_{proj} - \sum_k \gamma_k \Gamma_k \right], \quad (42)$$

where the thermodynamic meanings of the parameters γ_k, Γ_k can be fixed by thermodynamic correspondence. Again, the physical meaning of $\Theta, \beta_{proj}, \mu_{proj}$ and $N_{proj} = \Omega^{-1} N_k \Omega$ are also the "vacuum" of "dynamic part" of the corresponding parameters, which can be functional of variable of the coordinate of the system; when the k system in the ensemble tends to equilibrium, they tend to equilibrium H_k, β, μ and N_k , respectively. We want to emphasize again that in the book of Balescue^[19] the "dynamic part" means essence part of (irreversible) evolution of the density distribution, and the "vacuum" means without correlations. His work and Brussels-Austin school late works seem to show that the ρ_{proj} plays an important or influential role in the (irreversible) evolution of the system by extending it to the Rigged Hilbert space or Rigged Liouville space^[20]. Using this way can one build a corresponding relation between equilibrium statistical ensemble formalism and non-equilibrium statistical ensemble formalism? The answer is confirmed because the original Hamiltonian of the system has corresponding relation to the collision operator by the similarity transformation. Thus the dynamic variables Y are usually obtained by calculated over the non-equilibrium statistical distribution $\rho(\theta_k)$ which is given by the proposed non-equilibrium statistical ensemble formulas (32) or (40) or solution of the SKE (27), $\langle Y \rangle = Tr(Y\rho(\theta_k))$. If the second order approximation of Θ corresponds to the Master equation, the Boltzmann equation, the Pauli equation, or the Fokker-Planck equation, then $Tr(Y\rho(\theta_k))$ should deliver the expectation of corresponding physical value in the non-equilibrium ensembles. The Eq. (37) can be as starting base to get non-equilibrium statistical ensembles formulations for irreversibility, as demonstration of application below.

IV. APPLICATIONS

The ρ_{proj} can be a generalized reduced density operator by choosing an appropriate projector P defined as

$$\frac{\exp(-\beta H_B)}{Tr_B \exp(-\beta H_B)} Tr_B \rho = P \rho P, \quad (43)$$

with

$$P H_0 P = \frac{\exp(-\beta H_B)}{Tr_B \exp(-\beta H_B)} Tr_B H_0, \quad (44)$$

and $P + Q = 1$. Then the relations can be proved by assuming H_0 is diagonalized and H_{int} is off-diagonalized:

$$PHP = PH_0P, PH_{int}Q = 0, \quad (45)$$

$$PHQ = PH_{int}Q, PH_0Q = 0. \quad (46)$$

Thus, using Eqs.([?]) and ([?]), one can introduce

$$Q\Pi = C\Pi, \quad (47)$$

$$\Pi Q = \Pi P D. \quad (48)$$

This gives

$$\rho_{proj} = |P\Pi\phi\rangle \langle P\Pi\tilde{\phi}|, \quad (49)$$

which is just a kind of generalization of the reduced density operator for the open system. This means that a generalized Markovian (or non-markovian) equation for the generalized reduced density operator, ρ_{proj} , in quantum canonical ensembles can be given as the formula (37). For example a generalized Markovian equation may be derived by introducing $z^0 - QH_0Q$ to replace $z - QHQ$ in the creation operator C to cancel some memory effects of C ,

$$\rho_{proj} = \frac{\exp(-\beta_{proj}\Theta)}{Tr \exp(-\beta_{proj}\Theta)}, \quad (50)$$

with

$$\Theta = PHP + PHQ \frac{1}{z^0 - QH_0Q} QHP, \quad (51)$$

where z^0 is an eigenvalue of free Hamiltonian H_0 . Furthermore, a Markovian equation for the reduced density can be obtained by the second approximation with respect to the coupling number λ from the above equation,

$$\begin{aligned} \rho_{proj} &= (P + D) \rho (P + C) \\ &= \frac{\exp(-\beta_{proj}\Theta)}{Tr \exp(-\beta_{proj}\Theta)} \\ &\approx P\rho P + D\rho P + P\rho C + O(\lambda^4) \\ &\approx P\rho P + O(\lambda^2) \\ &= \frac{\exp(-\beta H_B)}{Tr_B \exp(-\beta H_B)} Tr_B \rho \\ &= \frac{\exp(-\beta_{proj}\Theta')}{Tr \exp(-\beta_{proj}\Theta')}, \end{aligned} \quad (52)$$

where

$$\Theta' = PHP + PHC, \quad (53)$$

$$\begin{aligned} C &= -i\lambda \int_0^{\pm\infty} d\tau U(\tau) QHP U(-\tau) \\ &= -i\lambda \sum_n \frac{1}{z_n^0 - QH_0Q} QHP, \end{aligned} \quad (54)$$

and

$$\beta_{proj} = P\beta P + O(\lambda^2). \quad (55)$$

As an application of the above formalism to the irreversibility, let us consider a Cayley tree system (immersed in a nose environment) subject to a strong interaction from environment or an external field. The Cayley tree is a loop-free network in which there exist three classes of nodes, they are (1) the root nodes, which is at origin of the tree and has connectivity m , (2) the nodes at interface with connectivity 1, and (3) the nodes below the interface with connectivity $m + 1$. Suppose that the network start from the root of the tree with nodes $i = 1$, and link it to m new nodes $i = 2, 3, \dots, m + 1$, one can indicates each node with a subsequent number, t_i indicating the time in which it arrives in the interface. At each time step, one can choose a node to grow, which gives rise to m new nodes. Consequently, the interface of the tree grows linearly in time, and the growing node is chosen at each time from the growing number of active nodes. In order to mimic the quenched noise of the medium^[22], one can assign to each node of the tree an "effective" energy θ_i corresponding to the intermediate operator Θ by considering the strong interaction from the environment, and require the higher energy nodes are more likely to grow than lower energy ones.

In fact, the total Hamiltonian of the Cayley tree system plus environment now is $H = H_0 + \lambda H_1$, where $H_0 = H_S + H_B$, H_S is Hamiltonian of the Cayley tree system, H_B is Hamiltonian of the environment and H_1 is supposed as an interaction part of the Hamiltonian H by coupling to the environment with coupling number $\lambda \gg 1$. This kind of system usually is difficult to treat using the perturbative method because the series of expansion of the perturbation approach is related to the power of λ , which is divergent. However, using the above proposed formula (37), a generalized reduced density operator for the Cayley tree system, ρ_{proj} , can be written as

$$i \frac{\partial \rho_{proj}(t)}{\partial t} = [\Theta, \rho_{proj}(t)] = [H_0 + \lambda H_1 C, \rho_{proj}(t)], \quad (56)$$

which can give

$$i\frac{\partial P}{\partial t} = P\Theta P = PH_0P + \lambda^2 PH_1G_QH_1P, \quad (57)$$

with

$$G_Q = \frac{1}{z - QHQ}. \quad (58)$$

By taking the Born expansion $G_Q = 1 + \lambda G_Q^0 H_1 + \lambda^2 G_Q^0 H_1 G_Q^0 H_1 + \dots$ one gets

$$P(\Theta - H_0)P = \lambda PH_1 \frac{1}{1 - \lambda G_Q^0 H_1} P. \quad (59)$$

When $\lambda \gg 1$, one obtain the corresponding eigenvalues of Θ as

$$\theta_n = \frac{1}{2} (z_n^0 + \langle \varphi_n | H_1 Q H_0 Q H_1^{-1} | \varphi_n \rangle), \quad (60)$$

where φ_n is the n th eigenvector of PH_0P , H_1^{-1} is an inverse operator of H_1 , and noticing $\langle \varphi_n | P\Theta P | \varphi_n \rangle = \theta_n$ is an eigenvalue for the open system (the Cayley tree) by P tracing out variables of the environment. Therefore the probability ρ_i for the active node i with energy θ_i to grow at time t can be given by

$$\rho_i = \frac{\exp\left(-\frac{\beta_{proj}}{2} (z_i^0 + \langle \varphi_i | H_1 Q H_0 Q H_1^{-1} | \varphi_i \rangle)\right)}{\sum_{j \in Int(t)} \exp\left(-\frac{\beta_{proj}}{2} (z_j^0 + \langle \varphi_j | H_1 Q H_0 Q H_1^{-1} | \varphi_j \rangle)\right)}, \quad (61)$$

where the model depends on the parameter β_{proj} , which can change characteristics of the tree. Comparing with the formula of ρ_i in original case^[22]

$$\rho_i = \frac{\exp(-\beta z_i^0)}{\sum_{j \in Int(t)} \exp(-\beta z_j^0)}, \quad (62)$$

it can be seen that the formula of this open system still has the similar structure as the original one except the shift of phase $\langle \varphi_j | H_1 Q H_0 Q H_1^{-1} | \varphi_j \rangle$ and $\beta \rightarrow \frac{\beta_{proj}}{2}$. This shows that a node i of the tree currently possesses an "effective" energy $\theta_i = z_i^0 + \langle \varphi_i | H_1 Q H_0 Q H_1^{-1} | \varphi_i \rangle$, from the original energy z_i^0 , corresponding to a random distribution $p(\theta)$. This allows the Cayley tree network to remain, with similar characteristic as that in the original case, if the interaction from environment can assign to each node, such as node i , of the tree an "effective" energy $\theta_i - z_i^0$ by keeping the original rule of forming Cayley tree (as a resource of self-orgnization).

Again, consider a quantum network whose nodes are composite by (electron) spins, $\sum_{\sigma} E_d n_d$, ($n_{d\sigma} = d_{\sigma}^{\dagger} d_{\sigma}$, d_{σ}^{\dagger} is creation operator of the spin) with interactions as connections. The environment (or control) field, $\sum_{k,\sigma} E_k n_{k\sigma}$,

($n_{k\sigma} = C_{k\sigma}^+ C_{k\sigma}$, $C_{k\sigma}^+$ is creation operator of the fermi particle) are composed by infinite (electron) fermis. The correlation between n_d is $Un_{d\uparrow}n_{d\downarrow} = \frac{U}{2} \sum_{\sigma} n_{d\sigma}n_{d\sigma}$, where U is correlation energy of electrons. The interaction between the network and the environment is $\lambda \sum_{k,\sigma} (C_{k\sigma}^+ d_{\sigma} + d_{\sigma}^+ C_{k\sigma})$, where λ is coupling number. Hence, the Hamiltonian operator is expressed by

$$H = \sum_{k,\sigma} E_k C_{k\sigma}^+ C_{k\sigma} + \sum_{\sigma} E_d d_{\sigma}^+ d_{\sigma} + Un_{d\uparrow}n_{d\downarrow} + \lambda \sum_{k,\sigma} (C_{k\sigma}^+ d_{\sigma} + d_{\sigma}^+ C_{k\sigma}). \quad (63)$$

When $\lambda = 0$, the free Hamiltonian of the network gives two energy levels as E_d and $E_d + U$. This allows the nodes of the network to be possibly in three combined status: 0 ($E_0 = 0$), 1 ($\sigma = \uparrow$ or \downarrow , $E_{1\sigma} = E_d$), and 2 ($\sigma = \uparrow$ and \downarrow , $2E_d + U$) occupations. Hence, following wolff transformation^{[?] [?]}, we introduce three projectors to divide the total Hilbert space as three subspaces:

$$P_0 = (1 - n_{d\uparrow})(1 - n_{d\downarrow}), \quad (64)$$

$$P_1 = n_{d\uparrow}(1 - n_{d\downarrow}) + n_{d\downarrow}(1 - n_{d\uparrow}), \quad (65)$$

$$P_2 = n_{d\uparrow}n_{d\downarrow}, \quad (66)$$

where P_n , $n = 0, 1, 2$ corresponds upon 0, 1, 2 occupations, with

$$P_n^2 = P_n, \quad (67)$$

$$P_n P_{n'} = 0. \quad (68)$$

Suppose that the total wave function Ψ is composed by ψ_0 , ψ_1 , ψ_2 in the three subspaces, respectively, then the Schrödinger equation $H\Psi = E\Psi$ can be expressed as

$$\begin{pmatrix} H_{00} & H_{01} & H_{02} \\ H_{10} & H_{11} & H_{12} \\ H_{20} & H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} \psi_0 \\ \psi_1 \\ \psi_2 \end{pmatrix} = E \begin{pmatrix} \psi_0 \\ \psi_1 \\ \psi_2 \end{pmatrix} \quad (69)$$

where $H_{nn'} = P_n H P_{n'}$, with

$$H_{02} = H_{20} = 0, \quad (70)$$

$$H_{01} = P_0 H P_1 = \lambda \sum_{k,\sigma} C_{k\sigma}^+ (1 - n_{d\sigma}) d_{\sigma}, \quad (71)$$

$$H_{12} = P_1 H P_2 = \lambda \sum_{k,\sigma} C_{k\sigma}^+ d_{\sigma} n_{d\sigma}. \quad (72)$$

When the nodes are in the 1 occupation, the local extra spins appear, which allows the network shows type of local magnetic effect as a self organization system. Thus cancelling ψ_0 and ψ_2 from Eq.(69) and considering Eqs.(70) -(72), we obtain the SKE as

$$\Theta_1 \psi_1 = E_1 \psi_1, \quad (73)$$

where the intermediate operator Θ_1 is given by

$$\Theta_1 = H_{11} + H_{12} (E - H_{22})^{-1} H_{21} + H_{10} (E - H_{00})^{-1} H_{01}. \quad (74)$$

In the second approximation with respect to λ , we have

$$H_{12} (E - H_{22})^{-1} H_{21} = \sum_{k,k',\sigma,\sigma'} \frac{\lambda^2}{U + E_d - E_{d'}} (-1) C_{k\sigma}^+ C_{k'\sigma'} d_\sigma n_{d\sigma} d_{\sigma'}^+ n_{d\sigma'}, \quad (75)$$

$$H_{10} (E - H_{00})^{-1} H_{01} = \sum_{k,k',\sigma,\sigma'} \frac{\lambda^2}{E_d - E_k} (-1) C_{k\sigma}^+ C_{k'\sigma'} d_{\sigma'}^+ (1 - n_{d\sigma'}) d_\sigma (1 - n_{d\sigma'}). \quad (76)$$

Considering $n_d = n_{d\uparrow} + n_{d\downarrow} = 1$, and $\hat{S}^z = \frac{1}{2} (d_\uparrow^+ d_\uparrow - d_\downarrow^+ d_\downarrow)$, $\hat{S}^+ = d_\uparrow^+ d_\downarrow$, $\hat{S}^- = d_\downarrow^+ d_\uparrow$, the Eqs.(75) and (76) become to

$$H_{12} (E - H_{22})^{-1} H_{21} = \sum_{k,k',\sigma,\sigma'} \frac{\lambda^2}{U + E_d - E_{k'}} \left\{ \left[\hat{S}^z (C_{k\uparrow}^+ C_{k'\uparrow} - C_{k\downarrow}^+ C_{k'\downarrow}) + \right. \right. \quad (77)$$

$$\left. \hat{S}^z C_{k\uparrow}^+ C_{k'\uparrow} + \hat{S}^- C_{k\uparrow}^+ C_{k'\downarrow} \right] - \frac{1}{2} \sum_{\sigma} C_{k\sigma}^+ C_{k'\sigma'} \right\},$$

$$H_{10} (E - H_{00})^{-1} H_{01} = \sum_{k,k'} \frac{\lambda^2}{E_k - E_d} \left\{ \left[\hat{S}^z (C_{k\uparrow}^+ C_{k'\uparrow} - C_{k\downarrow}^+ C_{k'\downarrow}) + \right. \right. \quad (78)$$

$$\left. \hat{S}^z C_{k\uparrow}^+ C_{k'\uparrow} + \hat{S}^- C_{k\uparrow}^+ C_{k'\downarrow} \right] + \frac{1}{2} \sum_{\sigma} C_{k\sigma}^+ C_{k'\sigma'} \right\}.$$

Replacing Eqs.(77), (78), and noticing $H_{11} \approx H_0 = \sum_{k,\sigma} E_k C_{k\sigma}^+ C_{k\sigma}$, Eq.(74) is given by

$$\Theta_1 = H_0 + H_p + H_{ed} \quad (79)$$

with

$$H_p = \sum_{k,k',\sigma} J_{kk'} C_{k\sigma}^+ C_{k'\sigma} \xrightarrow{U \rightarrow \infty} J \sum_{k,k',\sigma} C_{k\sigma}^+ C_{k'\sigma} \quad (80)$$

and

$$H_{ed} = - \sum_{k,k'} J_{kk'} \left\{ \hat{S}^z (C_{k\uparrow}^+ C_{k'\uparrow} - C_{k\downarrow}^+ C_{k'\downarrow}) + \hat{S}^z C_{k\uparrow}^+ C_{k'\uparrow} + \hat{S}^- C_{k\uparrow}^+ C_{k'\downarrow} \right\} \quad (81)$$

$$\xrightarrow{U \rightarrow \infty} -J \sum_{k,k'} \left\{ \hat{S}^z (C_{k\uparrow}^+ C_{k'\uparrow} - C_{k\downarrow}^+ C_{k'\downarrow}) + \hat{S}^z C_{k\uparrow}^+ C_{k'\uparrow} + \hat{S}^- C_{k\uparrow}^+ C_{k'\downarrow} \right\}, \quad (82)$$

where in the strong correlation condition, $U \rightarrow \infty$, we have

$$J_{kk'} = \frac{\lambda^2}{2} \left\{ \frac{1}{E_k - E_d} - \frac{1}{U + E_d - E_{k'}} \right\} \quad (83)$$

$$\xrightarrow{U \rightarrow \infty} J = -\frac{\lambda^2}{|E_d - E_F|}.$$

On the other hand, by means of the double time delay Green function (following ref.[23])

$$\langle\langle A(t); B(t') \rangle\rangle = -iu(t-t') \langle[A(t), B(t')]_+\rangle, \quad (84)$$

and the Furior transformation

$$\langle\langle A | B \rangle\rangle_\omega = \int dt e^{i\omega(t-t')} \langle\langle A(t); B(t') \rangle\rangle \quad (85)$$

one have

$$\omega \langle\langle A | B \rangle\rangle_\omega = \langle[A, B]_+\rangle + \langle\langle[A, H] | B \rangle\rangle_\omega, \quad (86)$$

$$\omega \langle\langle A | B \rangle\rangle_\omega = \langle[A, B]_+\rangle - \langle\langle[A, H] | B \rangle\rangle_\omega. \quad (87)$$

All these allows one to solve the Eq.(79) to obtain

$$\langle n_{d\uparrow} \rangle = \frac{1}{\pi} \operatorname{arccot} \left[\frac{E_d - E_F + U \langle n_{d\downarrow} \rangle}{\Gamma} \right], \quad (88)$$

$$\langle n_{d\downarrow} \rangle = \frac{1}{\pi} \operatorname{arccot} \left[\frac{E_d - E_F + U \langle n_{d\downarrow} \rangle}{\Gamma} \right], \quad (89)$$

where $\Gamma = V^2 \rho^{(0)}(E_F)$ represents half width, in which the energy of the system distribute around the resonance state $E_d + U \langle n_{d\downarrow} \rangle$ with width 2Γ , and the eigenvalue of the Θ is solved as a complex number

$$\theta_{d\sigma} = E_d + U \langle n_{d\downarrow} \rangle + i\Gamma.$$

When $E_d < E_F$, $E_d + U > E_F$, and $|E_d + U - E_F|, |E_d - E_F| \gg \Gamma$, there exist a local solution for the Eqs.(88) and (89): $\langle n_{d\uparrow} \rangle \rightarrow 1$, $\langle n_{d\downarrow} \rangle \rightarrow 0$, the network appears to have local magnetic vectors as a type of self-organization structure by interaction with huge nose environment. Its quantum statistical distribution in the (generalized) canonical ensemble can be given by previous formalsim as

$$\rho(\theta_{d\sigma}) = Z^{-1} e^{-\beta_{proj} \theta_{d\sigma}}, \quad (90)$$

and

$$Z = \sum_{d,\sigma} \exp(-\beta_{proj} \theta_{d\sigma}). \quad (91)$$

The irreversible generalized force and the entropy for the network system can be given by the above canonical partition function Z formulation, i.e.

$$Y = -\frac{1}{\beta} \frac{\partial}{\partial y} \ln Z, \quad (92)$$

and

$$S = k \left(\ln Z - \beta_{proj} \frac{\partial}{\partial \beta_{proj}} \ln Z \right), \quad (93)$$

which shows immediately that Y and S are complex since Z including complex eigenvalue $\theta_{d\sigma}$. This means that the entropy of this irreversible system is complex! Usually, the extension of the Hilbert space technique can be derived the complex spectrum for the self-adjoint operator, which demonstrates that the evolution of the intrinsic irreversible system has two semigroups to represent asymmetric time evolution, which have been discussed by many publications^[21]. What is new here, through constructing the non-equilibrium ensembles formulas, we simply reveal that the complex spectrum of the Θ can introduce complex entropy and complex generalized force, which should be a characteristic of irreversible system, and hard to find by using the equilibrium ensemble formalism of Gibbs.

V. CONCLUSIONS

In conclusions, we have proposed general non-equilibrium ensembles formalism based on the subdynamic equation. The constructed procedure is to use a similarity transformation between Gibbsian ensembles formalism based on the Liouville equation and the non-equilibrium ensemble formalism based on SKE. The obtained density distribution formula is a projected one that can represent essence part of (irreversible) evolution of the density distribution. Using this formulation, the irreversibility of the non-equilibrium system may emerge naturally as its entropy becomes complex, and can be exposed by calculating its general reduced density distribution.

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